Electro-Optical Characteristics of Au Nanostructures Fabricated by E-Beam Lithography

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Abstract The ITO electrodes and the gold alignment mark are patterned by optical lithography. Au nanorods are fabricated on the specific site of the ITO electrodes by the automatic alignments in electron beam (E-beam) lithography. The electro-potential of the Au nanorods is tuned by applying various currents through the ITO electrode and therefore the plasmon resonance frequency of Au nanorods is shifted, which is probed by microscopic scattering spectroscopy. Conversely the electric conductivity of the ITO electrode is dependent on the polarization of the plasmon resonance.

Plasmon resonance describes the phenomenon that free electrons in the conduction band are excited and resonate with the applied electromagnetic field. Plasmon resonance can be experimentally observed in Au nanostructures made by either chemical synthesis or electron beam lithography. The resonance wavelength can be found from the absorption spectrum of bulk solutions or the scattering spectrum of single Au nanostructures. It has been found the plasmon resonance wavelength can be affected by changing the properties of the vicinity of Au nanostructure such as refractive index[1]. Henglein *et al* and Mulvaney[2,3] observed that plasmon resonance peak of silver nanoparticles can also be blue-shifted by injecting electrons as the bulk plasma frequency of metal is proportional to the free electron density in nanoparticles. In this paper, 30nmx45nm Au nanorods are created by E-beam lithography on ITO electrodes which is pre-patterned in optical lithography. The electro-potential of the Au nanorods is tuned by applying various currents through the ITO electrodes. The plasmon resonance frequency of the Au nanorod shifts because of the electron injection. On the other hand, the conductivity of the ITO electrodes is affected by the polarized plasmon resonance.

The schematic diagram of the device is shown in Fig. 1, respectively. An ITO channel is patterned on a quartz substrate. An Au nanorod sits above the ITO channel. Electrons are injected into the Au nanorod by applying the voltage potential on the opposite ITO electrodes. The plasmon resonance is induced by the illumination of polarized white light from oblique angles and the scattering light is collected by a microscope objective to a spectrophotometer.

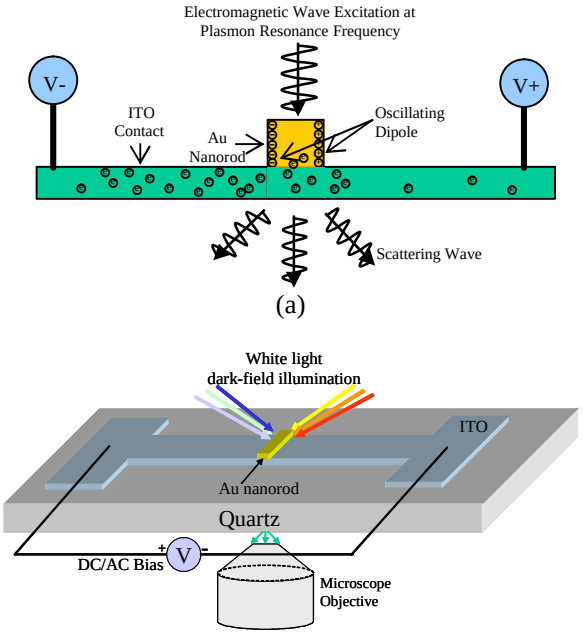


Fig. 1 (a) Cross section view and (b) Top view of the device of Au nanorod on an ITO electrode

The fabrication process of such device is illustrated in Fig. 2. It includes both optical and E-beam lithography. The optical lithography process is described as followed. A 100nm thick ITO layer is firstly sputtered on a quartz wafer. The ITO electrode is patterned on the quartz substrate by optical lithography and wet etching. The etching is done in the mixture of 20% HCl and 5% HNO_3 at 55 ^oC for 2 minutes. Au contact

pads and alignment marks are then made by the second step of optical lithography, E-beam evaporation of Au and the following lift off process. The alignment marks are prepared for the use in E-beam writing since the ITO channel and Au nanorods are to be placed on the specific positions on the wafer. Till this step the wafer is ready for the following E-beam lithography.

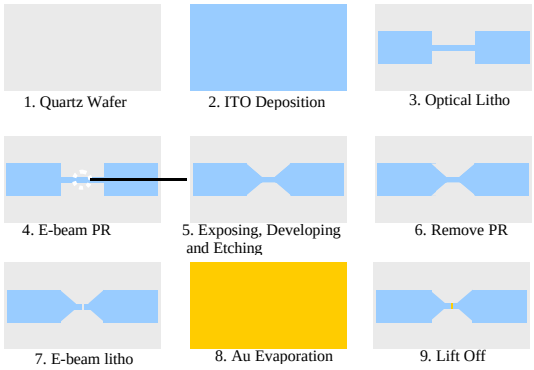
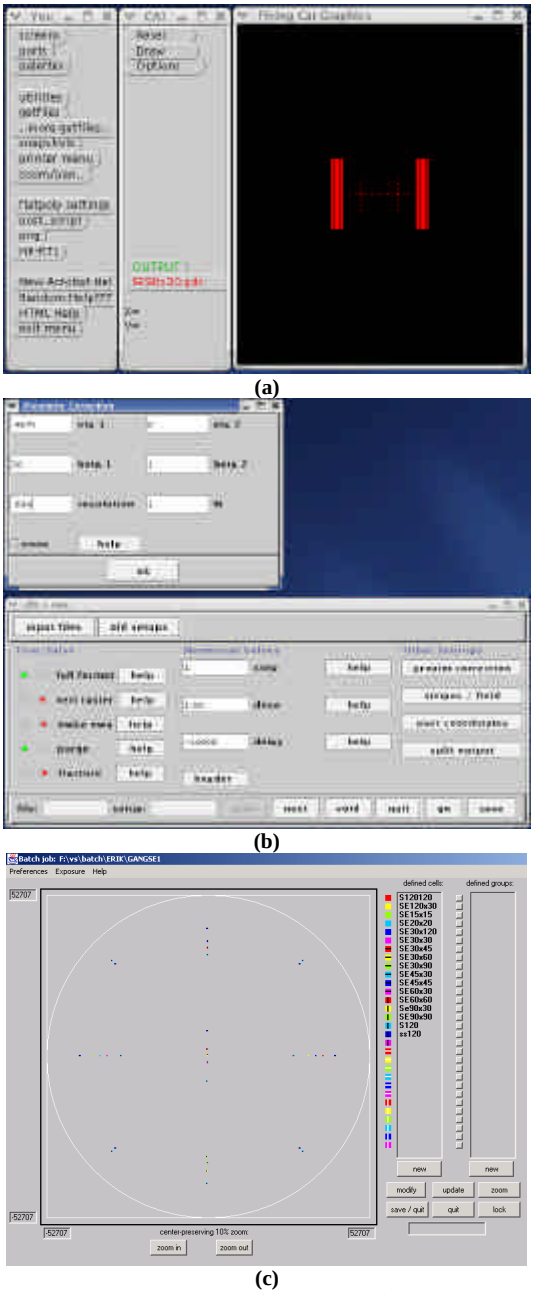


Fig. 2 Fabrication process

The device is made by two times of E-beam lithography. Firstly the ITO nano channel is created and subsequently the Au nanorod is created on the ITO channel. Designs including patterns to be written as well as the alignment mark are laid out and converted into GDSII files. CATS (Fig. 3a) is used to fracture and flatten the design file and CFLT-NWX (Fig. 3b) is used for the conversion into the NWX files which are recognizable by the E-beam writer. The alignment marks are also converted into NWT files, the alignment template. The basic design blocks are then arranged on specific locations on a 4'' wafer using VSEDIT (Fig. 3c). The corresponding alignment marks are also designated at this step. The parameters ?, and ß for the proximity correction are found prior to the E-beam writing to be $h = 0.4675$ and $b = 30$. These parameters are included in the CAD designs.

The photoresist, 1% MW950 PMMA in chlorobenzene, is spun on the wafer at the speed of 2000 RPM resulting a 59.6 nm thickness. After 30 minutes of pre-exposure bake in 170 ^{o}C convection oven, the wafer is loaded into the E-beam writer. The energy of the electron beam is set to 1000 µC/cm^2. The writing minor and major fields are 4.096µm x 4.096µm and 262.144µm x 262.144µm, respectively. The wafer is aligned manually on the stage according to the alignment marks in three different major fields before the automatic alignment and writing. After writing, the wafer is developed in a solution of 1:3 MIBK to IPA for 30 seconds.



(a)

(b)

(c)

Fig. 3 Graphical User Interface (GUI) of **(a)** CATS, **(b)** CFLT-NWX, and **(c)** VSEDIT

Fig. 4 shows the micrograph of the device after first time of E-beam lithography. A 30nm wide channel is created on a 10µm channel defined by optical lithography. The wafer is then subject to etching to remove excess ITO.

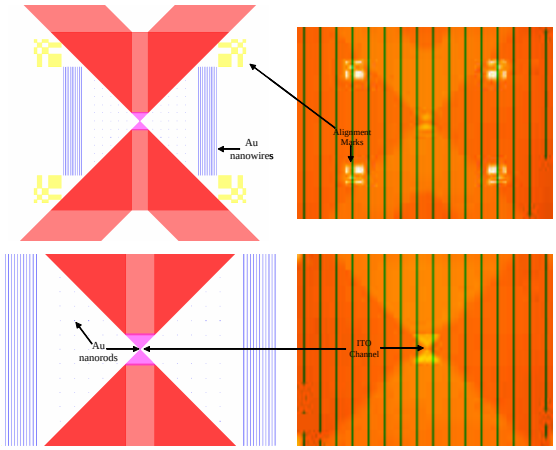


Fig. 4 Layout (left) and micrograph of the device after the ITO channel is created in the first time E-beam lithography (right). Upper row and lower row are shown in larger and smaller fields of view, respectively.

A new layer of PMMA resist is spun on after stripping the developed PMMA resist. The wafer is then subject to the second time of E-beam lithography. The alignment procedure is the same as the first time. The patterns of nanorods and nanowires are created on PMMA as shown in Fig. 5. The widths of nanowires range from 20 nm to 150 nm and their lengths are 200 μm. The nanorods have various shapes in different fields and those shown in Fig.4 are 30nm x 30nm nanorods.

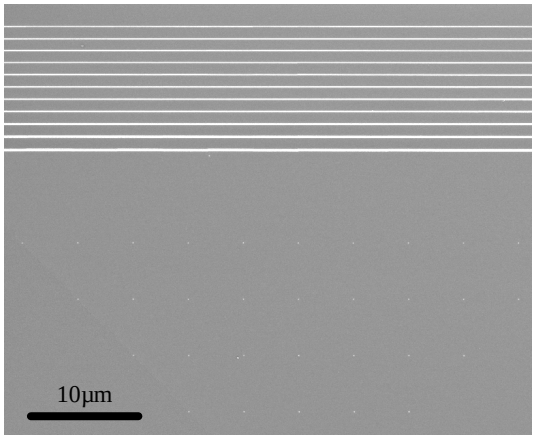
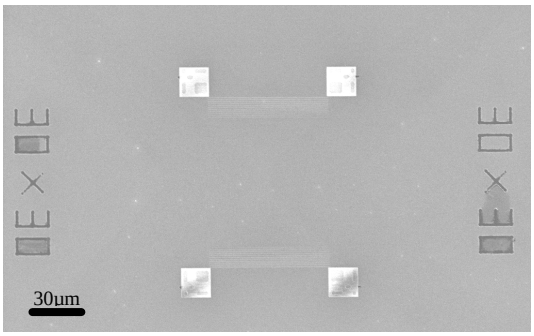
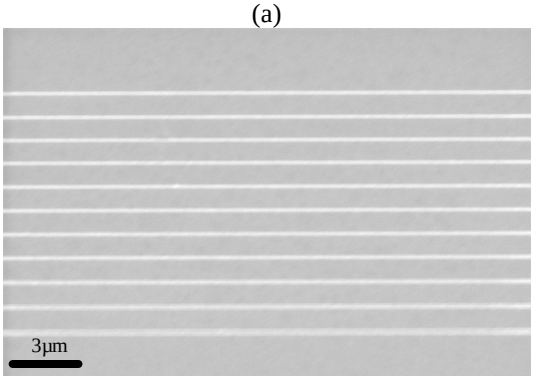


Fig.5 Nanowires and nanorods patterns on PMMA.

After the second time of E-beam writing, the wafer is hard baked on a 100 ^{o}C hot plate for 90 seconds followed by the descum in oxygen plasma for 15 seconds. 50 nm Au layer is then evaporated on the wafer, prior to which 5nm Cr layer is deposited to increase adherence to the ITO substrate. The subsequent lift off process is carried out in the bath of acetone with ultrasonic agitation. The SEM of the device, Au nanowires and 30nmx30nm nanorods are shown in Fig. 6.



(a)



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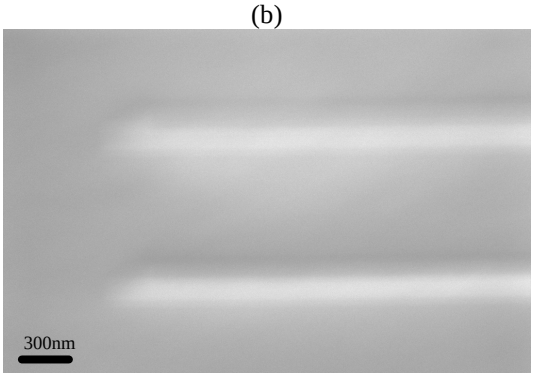

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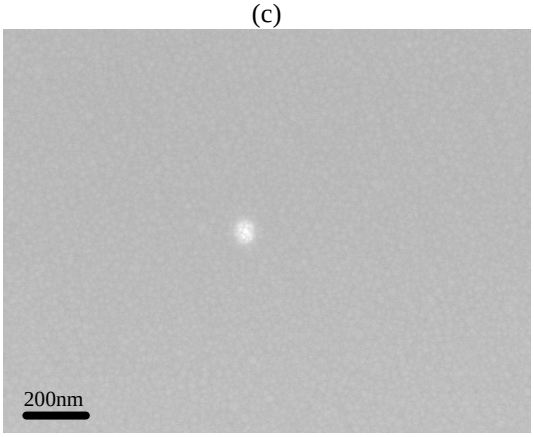
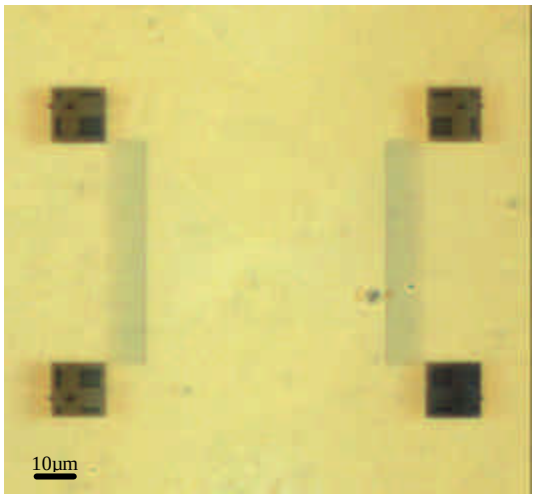


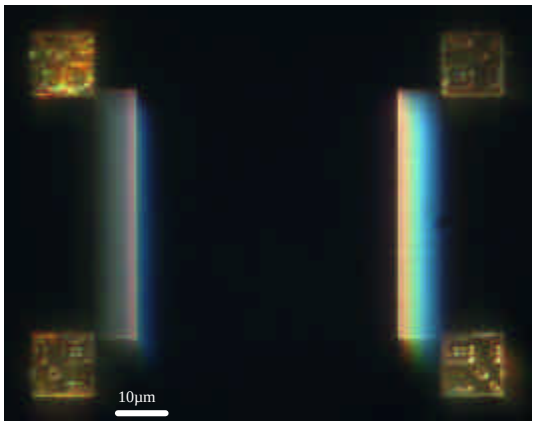
(d)

Fig. 6 SEM of **(a)** the device, **(b)** and **(c)** Au nanowires, and **(d)** 30nmx30nm Au nanorod

The finished wafer is diced and two electrical wires are connected to the contact pad of a device. The comparisons of the bright-field and dark-field scattering image of the device are illustrated in Fig. 7. Different colors exhibit for the Au nanowires in different widths with the excitation light polarized along the nanoscale short axes of the nanowires. Au nanowires whose widths are larger than 80nm exhibit reddish colors, those small than 80nm but larger than 50nm exhibit yellowish or greenish colors and those smaller than 50nm Au nanowires exhibit bluish or even purple colors.



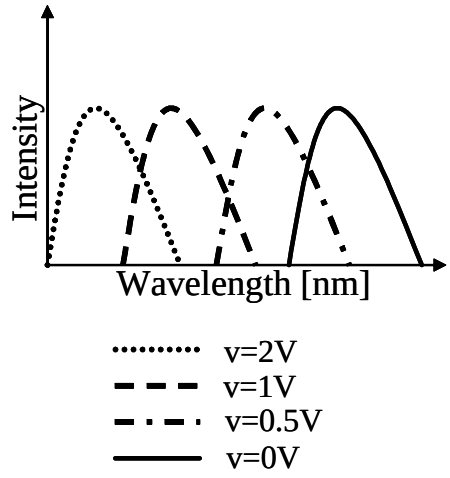
(a)



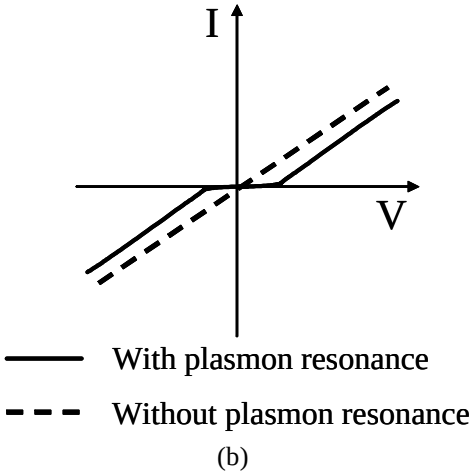
(b)

Fig. 7 (a) Bright field and (b) dark-field scattering images of the Au nanowires and nanorods (not clear)

The electro-optical characterization experiment is still on-going by the time the report is written. The expected results are shown in Fig. 8. The current through the ITO channel is measured synchronically with the scattering spectra of the Au nanowires and nanorods. Very distinct I-V characteristics of the ITO channel exhibit with and without inducing plasmon resonance on the Au nanowires and nanorods. Coulomb blockade is observed as the resonant electron induced oscillating dipole forms a coulomb gap with a very large double-layer capacitance. On the other hand, the plasmon resonance peak wavelength shifts when free electrons are injected to the Au nanowire, and the shift corresponds to the variation of the electric current through the channel.



(a)



(b)

Fig. 8 (a) Plasmon resonance shift of the Au nanowire with applied voltage bias on the ITO channel. (b) I-V characteristic curve of the structure. Coulomb Blockade phenomenon is observed.

Reference

1. G. L. Liu, V. B. Rodriguez, and L. P. Lee, (*unpublished*)
2. A. Henglein, P. Mulvaney, and T. Linnert, *J. Chem. Soc. Faraday Discuss*, **92**, 31 (1991)
3. P. Mulvaney, *Langmuir*, **12**, 791 (1996)